Electronic Supporting Information (ESI)

Highly Selective Separation of Carbon Dioxide from Nitrogen and Methane by Nitrile/Glycol-Difunctionalized Ionic Liquids in Supported Ionic Liquid Membranes (SILMs)

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CHALLENGES IN SYNTHESIS AND PURIFICATION

The tertiary amines used in the syntheses have been functionalized with a nitrile and an oligo(ethylene oxide) groups in separate steps. The quaternisation reaction always took place in acetonitrile, as this solvent provided the best yields in comparison with tetrahydrofuran, toluene, dichloromethane or ethyl acetate. In each case, the ionic liquids had to be purified after the quaternisation reaction. Since the compounds were too polar to be chromatographed on silica gel or alumina, the impurities were removed by solvent extraction. The ionic liquids were dissolved in a large amount of water (for example 300 mL of water for 10 g of ionic liquid) and washed with three small portions of dichloromethane (for example 3 times 10 mL). Unfortunately, this practice led to lower yields, since the ionic liquid has also a significant solubility in dichloromethane. To obtain a *p*-toluenesulfonate rather than a bromide ionic liquid, the first step involved in most cases the preparation of a tertiary amine containing a nitrile group. Then, this compound was quaternised with an equivalent (or an excess) of triethyleneglycol monomethylether *p*-toluenesulfonate or two equivalents (or an excess) of triethyleneglycol di-*p*-toluenesulfonate to yield a tosylate (dicationic) ionic liquid.

SYNTHESES OF IONIC LIQUIDS PRECURSORS

1-(3-Cyanopropyl)imidazole

The synthesis was based on the literature procedure.[1] Sodium imidazolate (1.34 g, 14.9 mmol) was added to THF, and the slurry was stirred at room temperature for 1 hour or until a uniform suspension was obtained. Then 4-(*N*)-pyrrolidinylbutyronitrile (1.35 mL, 13.5 mmol) was added and the mixture was refluxed at 65 °C for 20 hours. After this time, the reaction was stopped, allowed to cool, the solids were filtered off and washed with THF. The solvent was evaporated and the crude product was dissolved in 150 mL of dichloromethane. Three spoons of $MgSO_4$ and one spoon of activated carbon were added to the mixture. It was stirred 5 min and filtered through a basic activated Al_2O_3 pad and washed with dichloromethane. After evaporation *in vacuo*, yellow oil was obtained in purity sufficient for subsequent reactions. Yield: 1.80 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.11 (s, 1H), 6.94 (s, 1H), 4.15 (t, 2H, *J* = 6.4 Hz), 2.32 (t, 2H, *J* = 6.6 Hz), 2.14 (m, 2H, *J* = 6.6 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.1, 130.2, 118.6, 44.9, 26.8, 14.4 ppm. IR (ATR, cm^{-1}): 2942, 2247 (nitrile), 1507, 1447, 1288, 1108, 1079, 1031, 908, 821, 742, 664, 624.

1-(Cyanomethyl)imidazole:

Imidazole (2.5 g, 36.7 mmol) was mixed with bromoacetonitrile (2.56 mL, 36.7 mmol) and K_2CO_3 (5.58 g, 40.4 mmol) in acetonitrile and stirred at 65 °C for 30 min. The stirring was continued at room temperature for the next 20 h. The mixture was then filtrated and the solvent evaporated. Column chromatography on silica gel with dichloromethane:ethanol (95:5) as eluent yielded the product, brown crystals. Yield: 2.93 g (75%). M.p.: 50 °C. ^{1}H NMR (300MHz, $CDCl_3$): δ = 7.59 (s, 1H), 7.17 (s, 1H), 7.06 (s, 1H), 4.91 (s, 2H) ppm. ^{13}C

NMR (75MHz, $CDCl_3$): δ = 137.0, 131.2, 118.9, 113.5, 34.4 ppm. IR (ATR, cm^{-1}): 2875, 2259 (nitrile), 1644, 1502, 1422, 1285, 1232, 1106, 1076, 1027, 905, 740, 659, 615, 481.

Preparation of 1-(10-Cyanodecyl)imidazole[2]

Sodium imidazolate (1.07 g, 11.9 mmol) was added to THF, and the slurry was stirred at room temperature for 1 hour or until a uniform suspension was obtained. Then 11-bromoundecanenitrile [2] (2.50 g, 10.2 mmol) was added and the mixture was refluxed at 65 °C for 20 h. After this time, the reaction was stopped, allowed to cool, and the solids were filtered off and washed with THF. The solvent was evaporated and the crude product was dissolved in 150 mL of dichloromethane. Three spoons of $MgSO_4$ and one spoon of activated carbon were added to the mixture. It was stirred 3 min and filtered through a basic activated Al_2O_3 pad and washed with dichloromethane. Removal of the solvent *in vacuo* yielded yellow oil. Yield: 1.32 g (56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (s, 1H), 7.06 (s, 1H), 6.90 (s, 1H), 3.92 (t, 2H, *J* = 7.06 Hz), 2.33 (t, 2H, *J* = 7.09 Hz), 1.84-1.71 (m, 2H), 1.71-1.56 (m, 2H), 1.50-1.38 (m, 2H), 1.37-1.17 (m, 10H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.0, 129.3, 119.8, 118.8, 31.0, 29.2, 29.1, 29.0, 28.7, 28.6, 26.5, 25.3, 17.1 ppm. IR (ATR, cm^{-1}): 2926, 2855, 2244 (nitrile), 1566, 1507, 1462, 1359, 1282, 1228, 1169, 1108, 1078, 1032, 907, 813, 731, 664, 625.

NMR SPECTRA

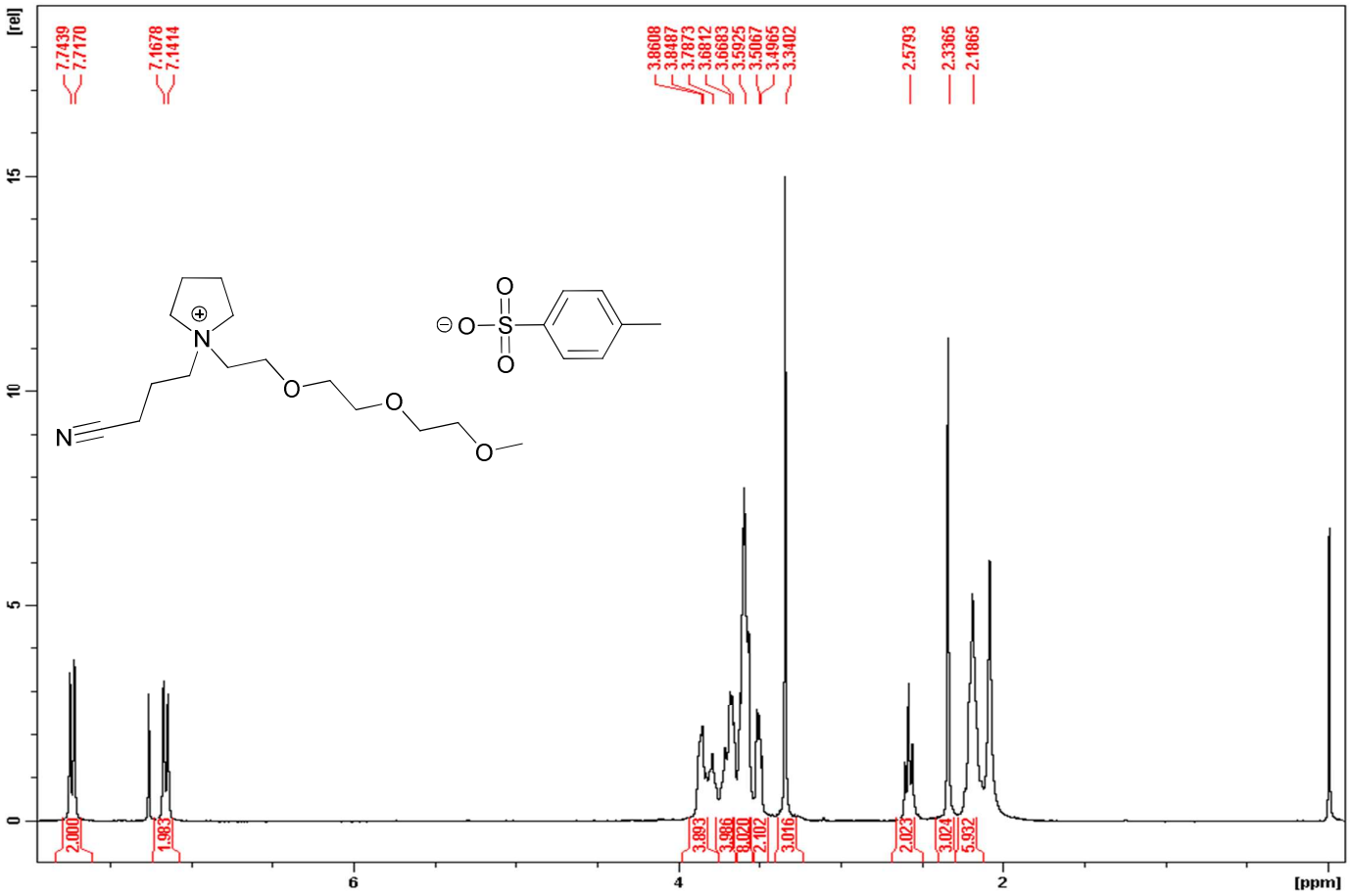

Figure S1 ^{1}H NMR spectrum of 1-(3-Cyanopropyl)-1-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]pyrrolidinium *p*-toluenesulfonate (1a).

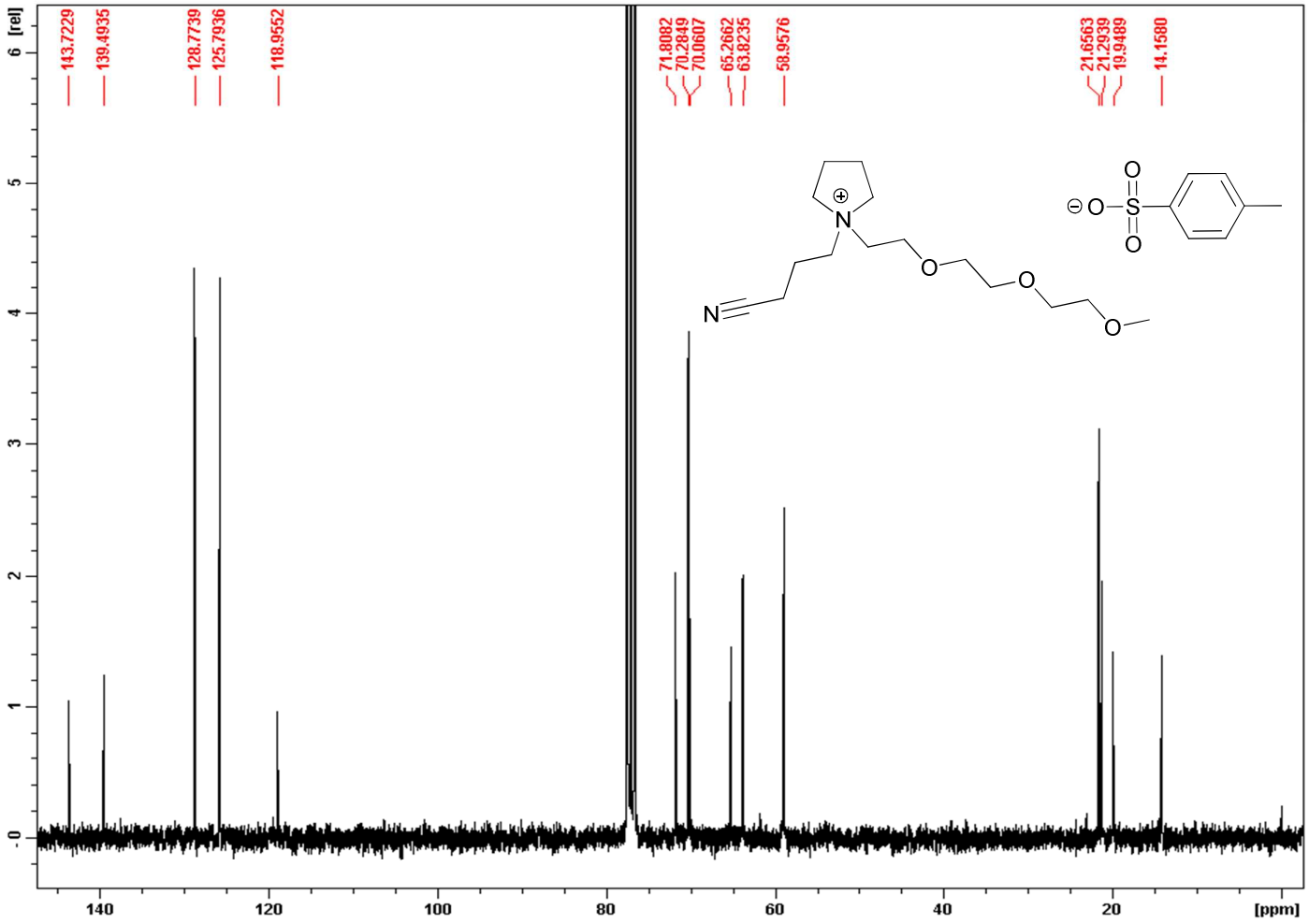

Figure S2 ^{13}C NMR spectrum of 1-(3-Cyanopropyl)-1-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]pyrrolidinium *p*-toluenesulfonate (1a).

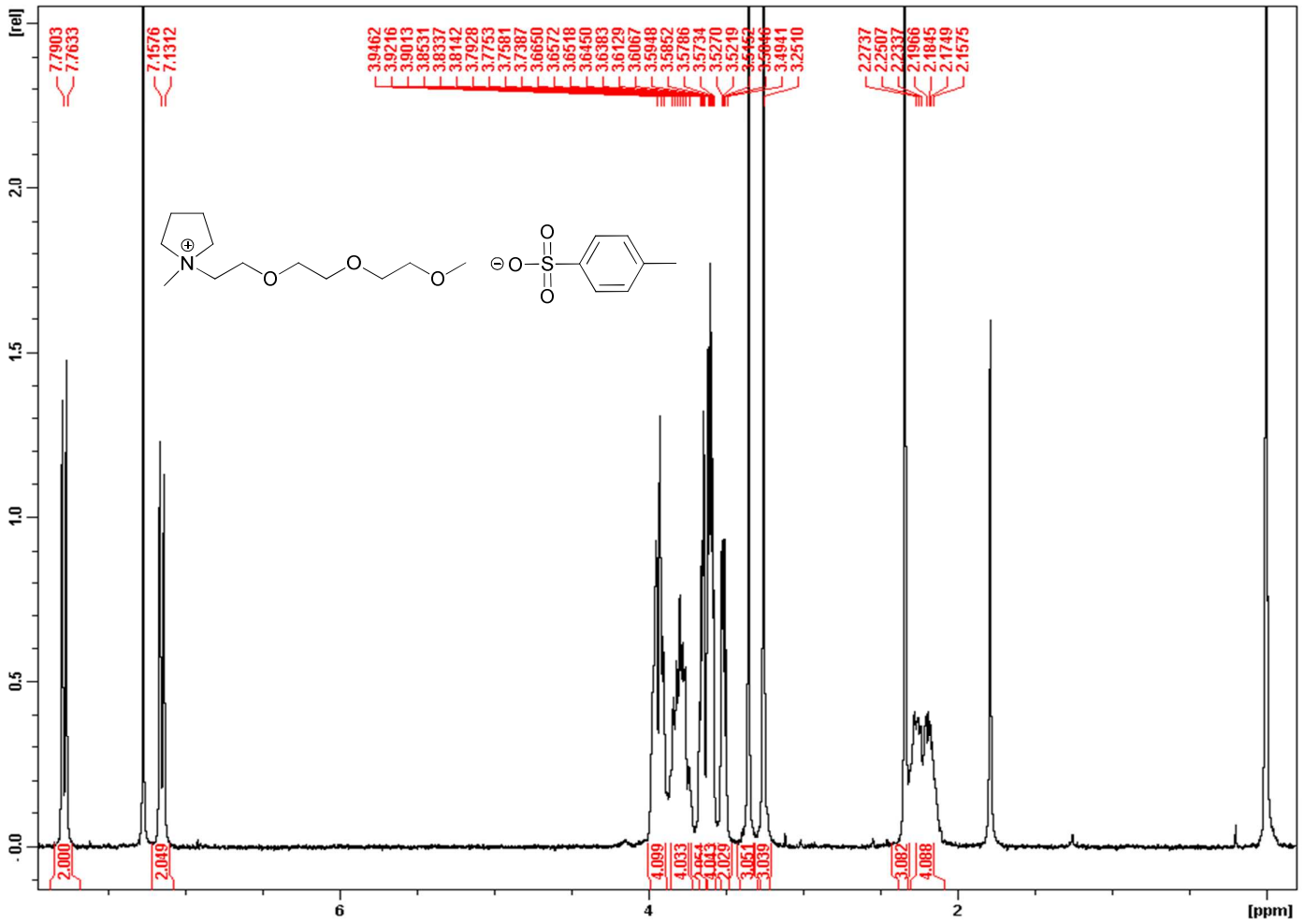

Figure S3 ^{1}H NMR spectrum of 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidinium *p*-toluenesulfonate (1b).

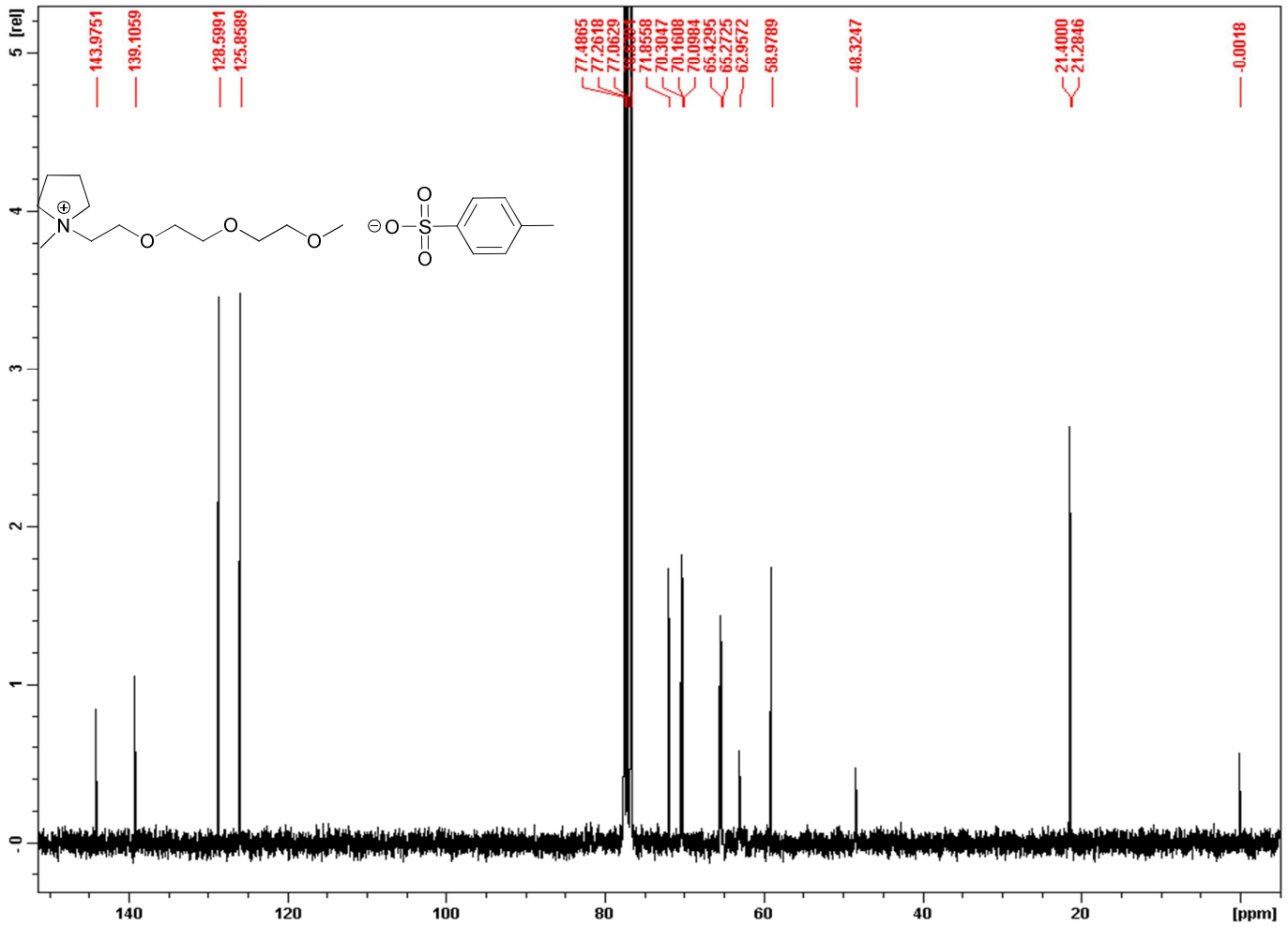

Figure S4 ^{13}C NMR spectrum of 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylpyrrolidinium *p*-toluenesulfonate (1b).

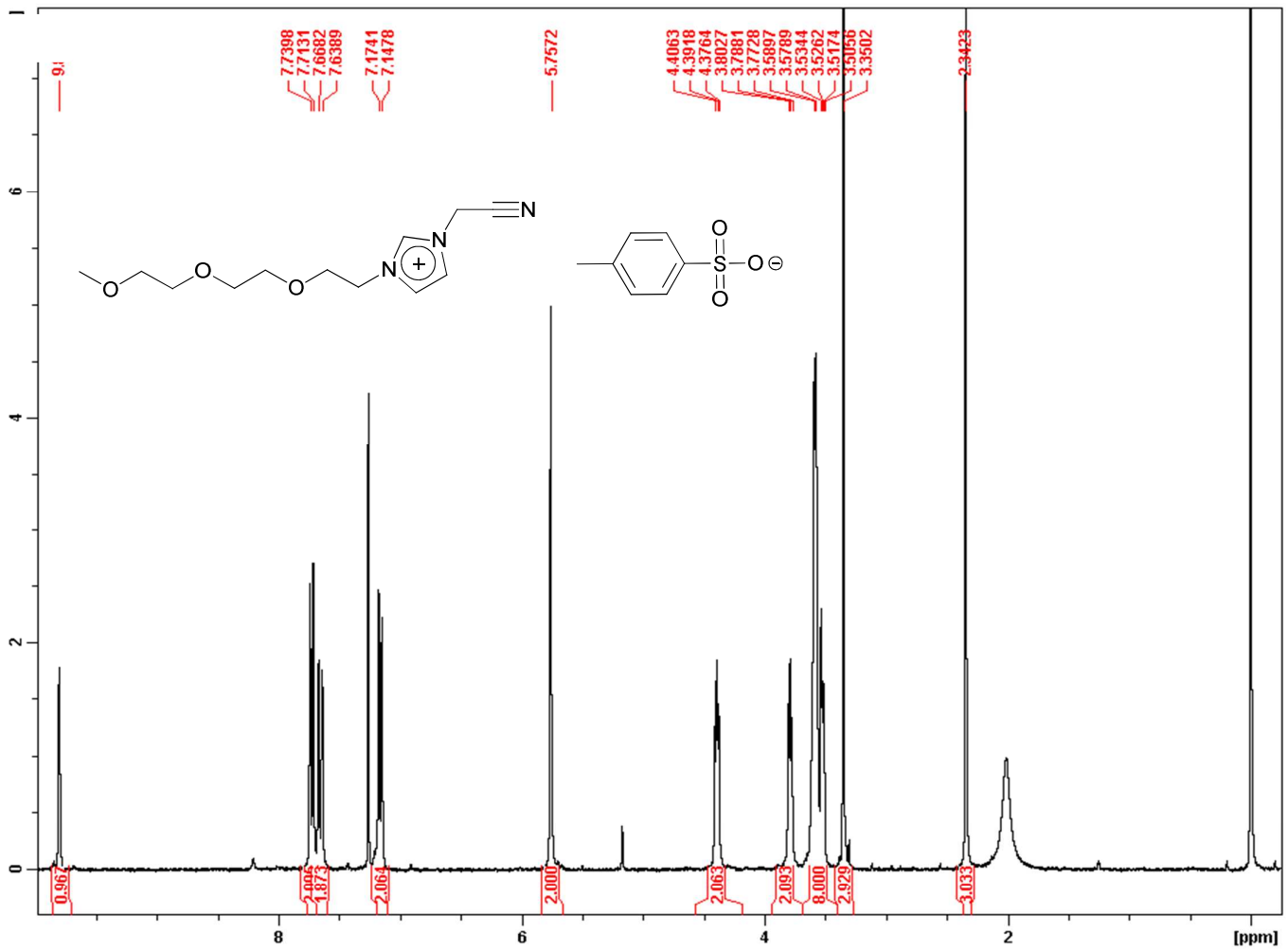

Figure S5 ^{1}H NMR spectrum of 1-(Cyanomethyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium *p*-toluenesulfonate (2a).

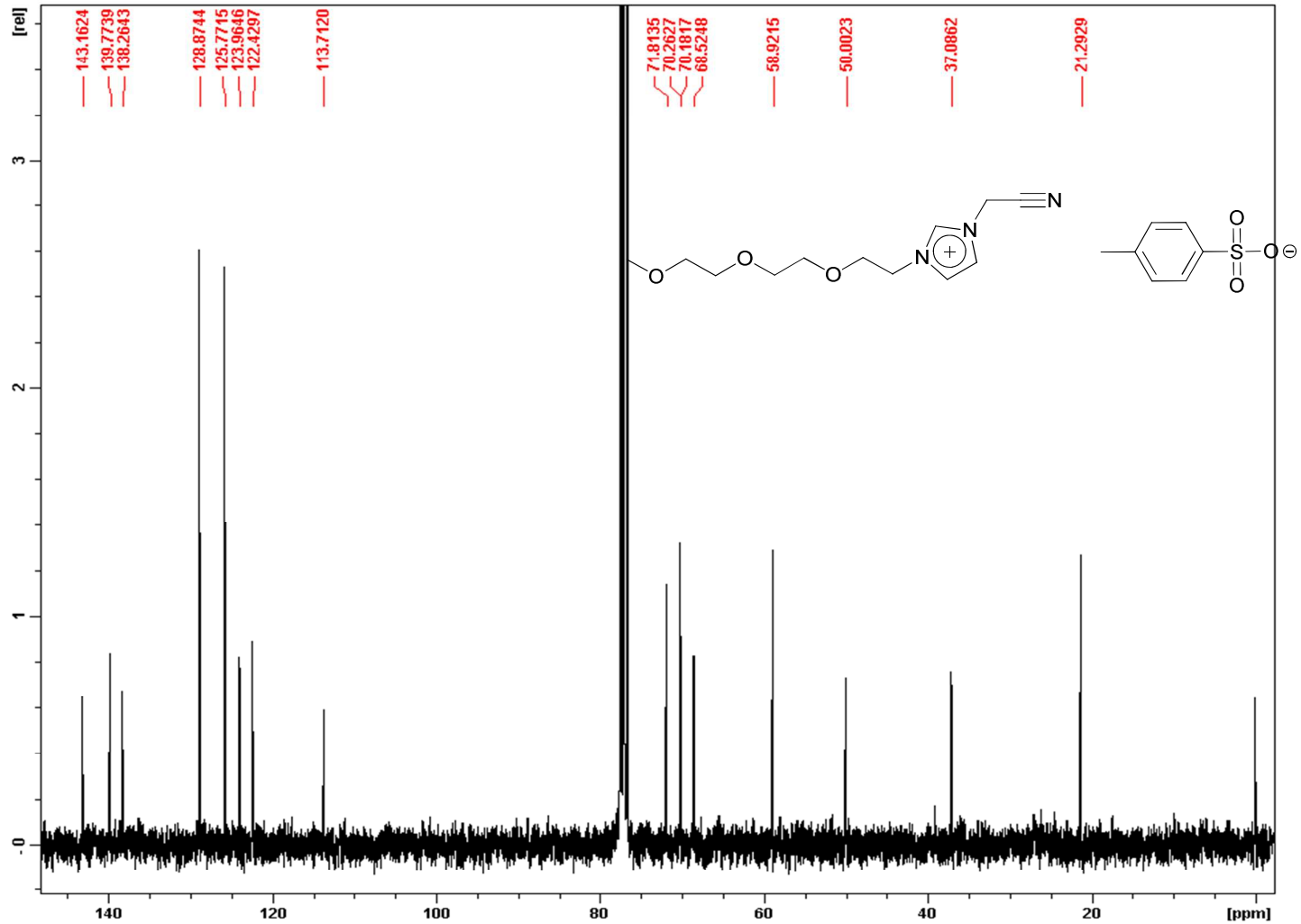

Figure S6 ^{13}C NMR spectrum of 1-(Cyanomethyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium *p*-toluenesulfonate (2a).

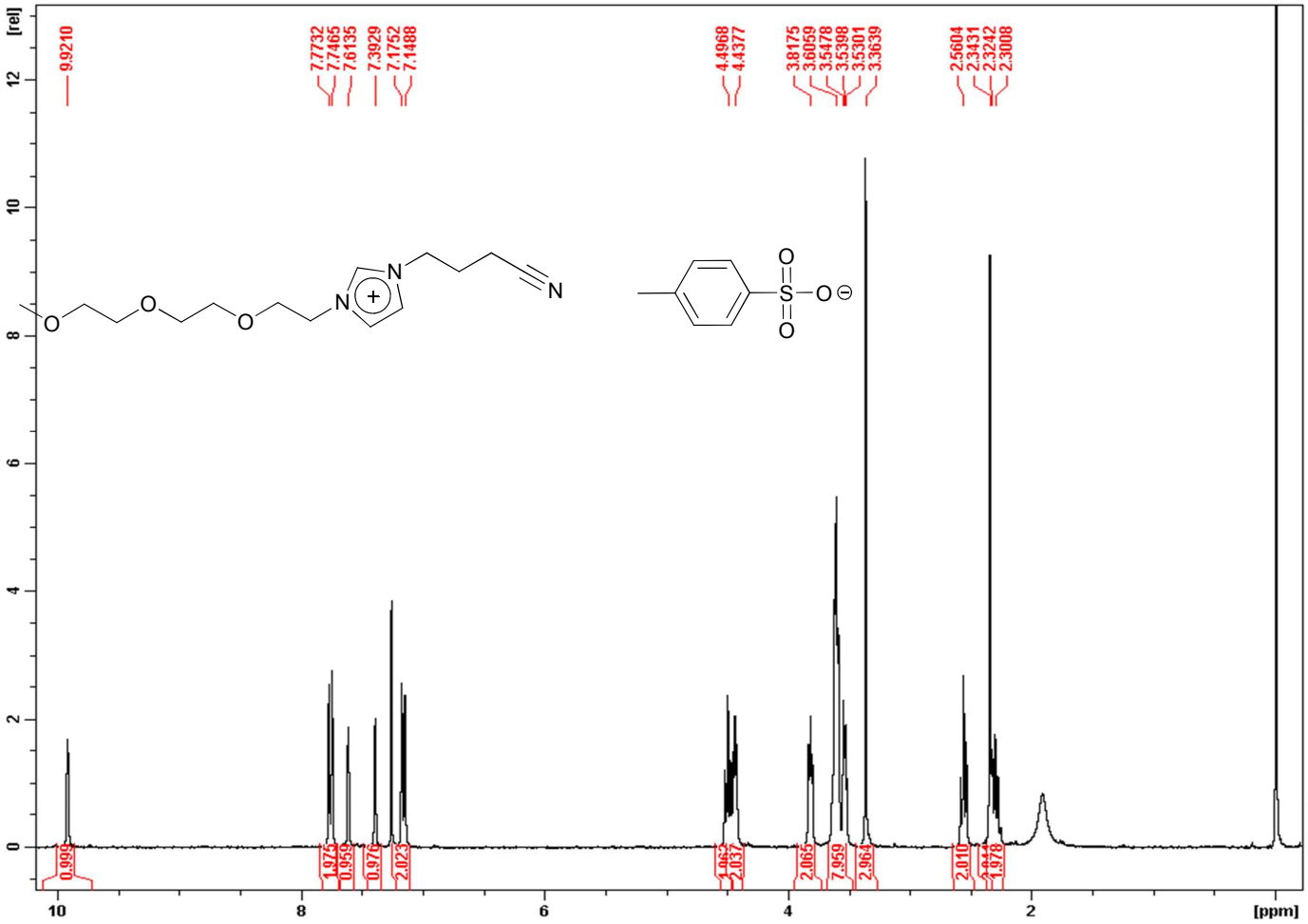

Figure S7 ^{1}H NMR spectrum of 1-(3-Cyanopropyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium *p*-toluenesulfonate (2b).

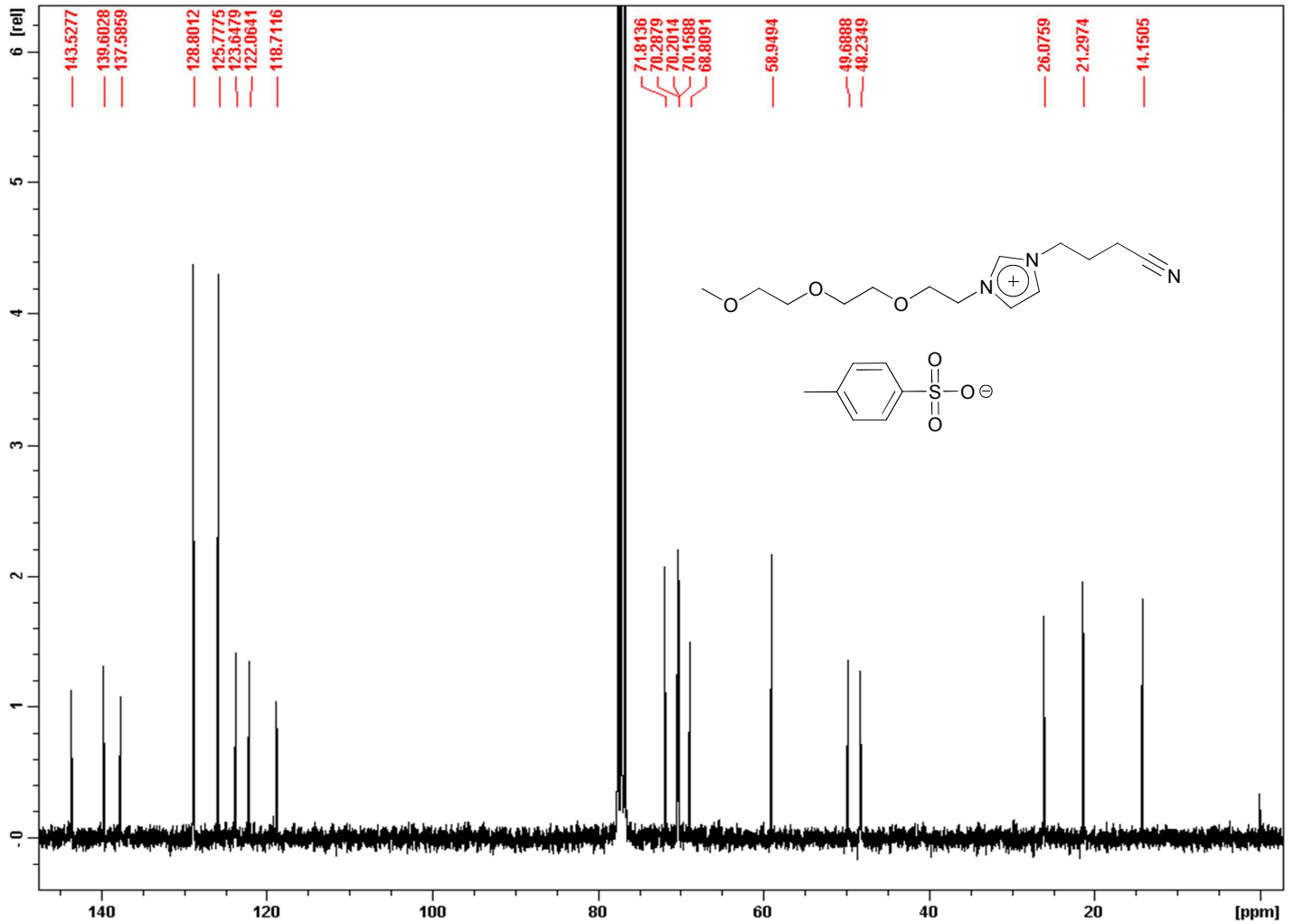

Figure S8 ^{13}C NMR spectrum of 1-(3-Cyanopropyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium *p*-toluenesulfonate **(2b)**.

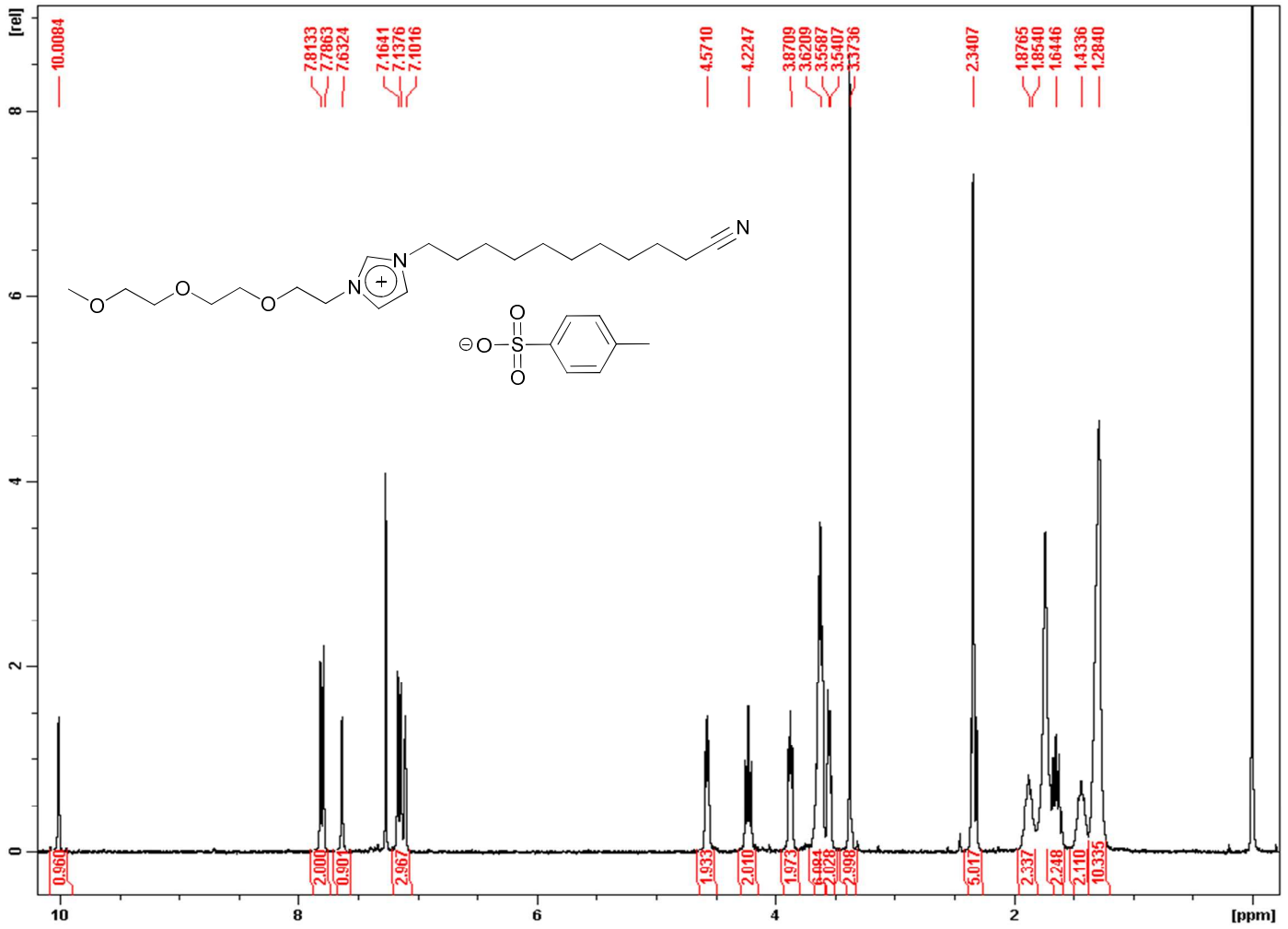

Figure S9 ^{1}H NMR spectrum of 1-(10-Cyanodecyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium p-toluenesulfonate (2c).

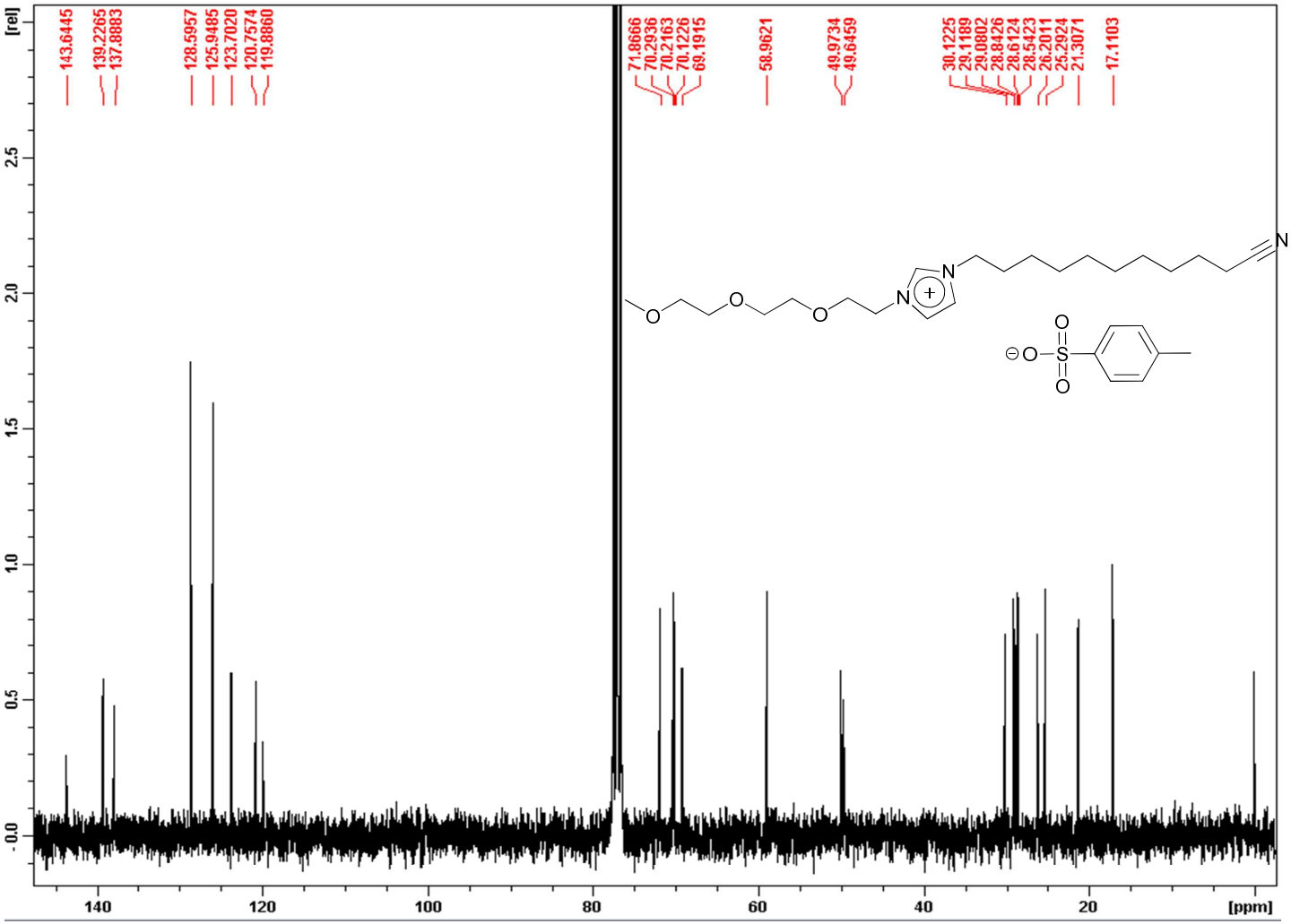

Figure S10 ^{13}C NMR spectrum of 1-(10-Cyanodecyl)-3-[2-[2-(2-methoxyethoxy)ethoxy]ethyl]imidazolium p-toluenesulfonate **(2c).**

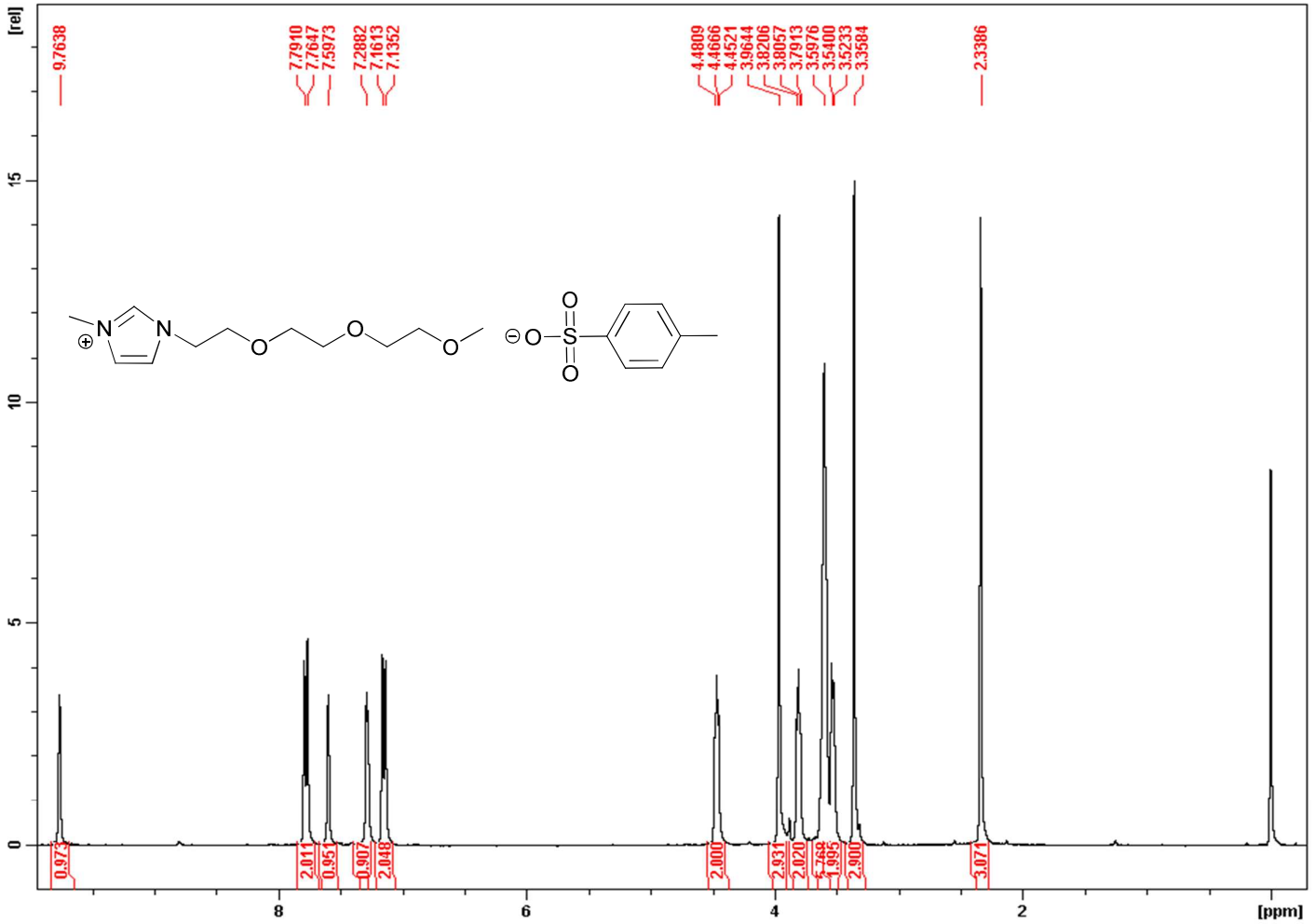

Figure S11 ^{1}H NMR spectrum of 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylimidazolium *p*-toluenesulfonate (2d).

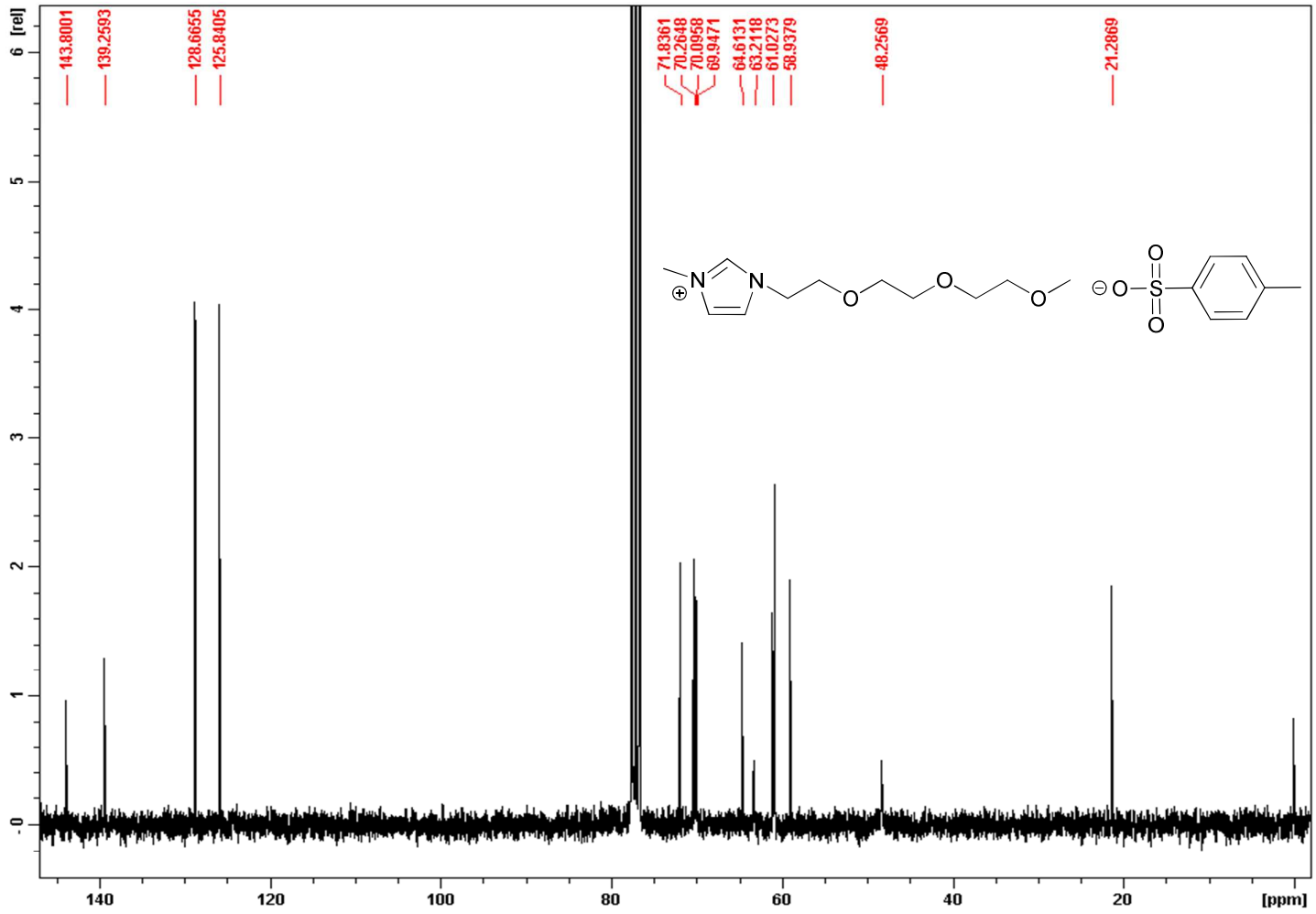

Figure S12 ^{13}C NMR spectrum of 1-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-1-methylimidazolium *p*-toluenesulfonate (2d).

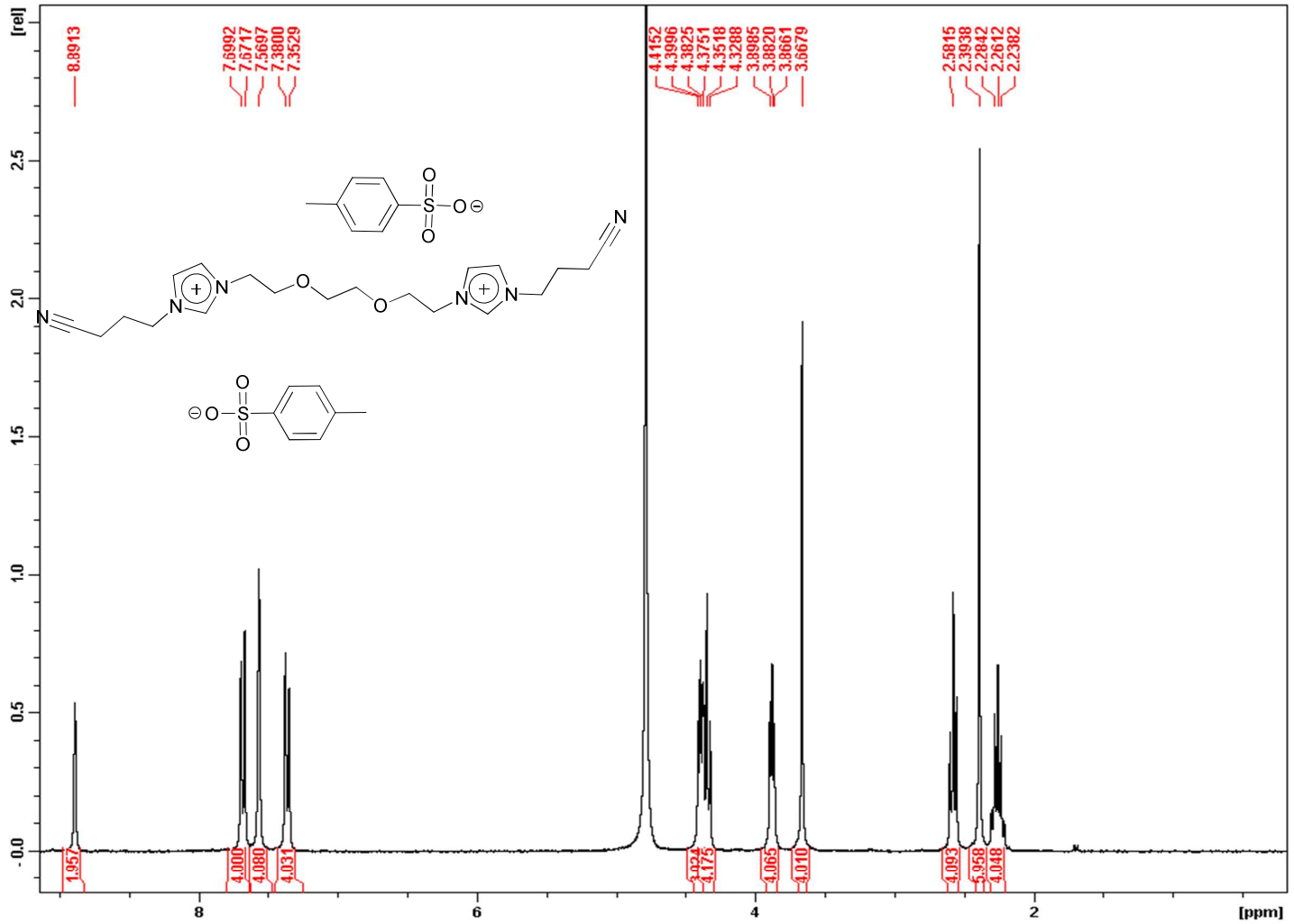

Figure S13 ^{1}H NMR spectrum of 1,8-Bis[1-(3-cyanopropylimidazolium-1-yl)]-3,6-dioxaoctane di(p-toluenesulfonate) (3).

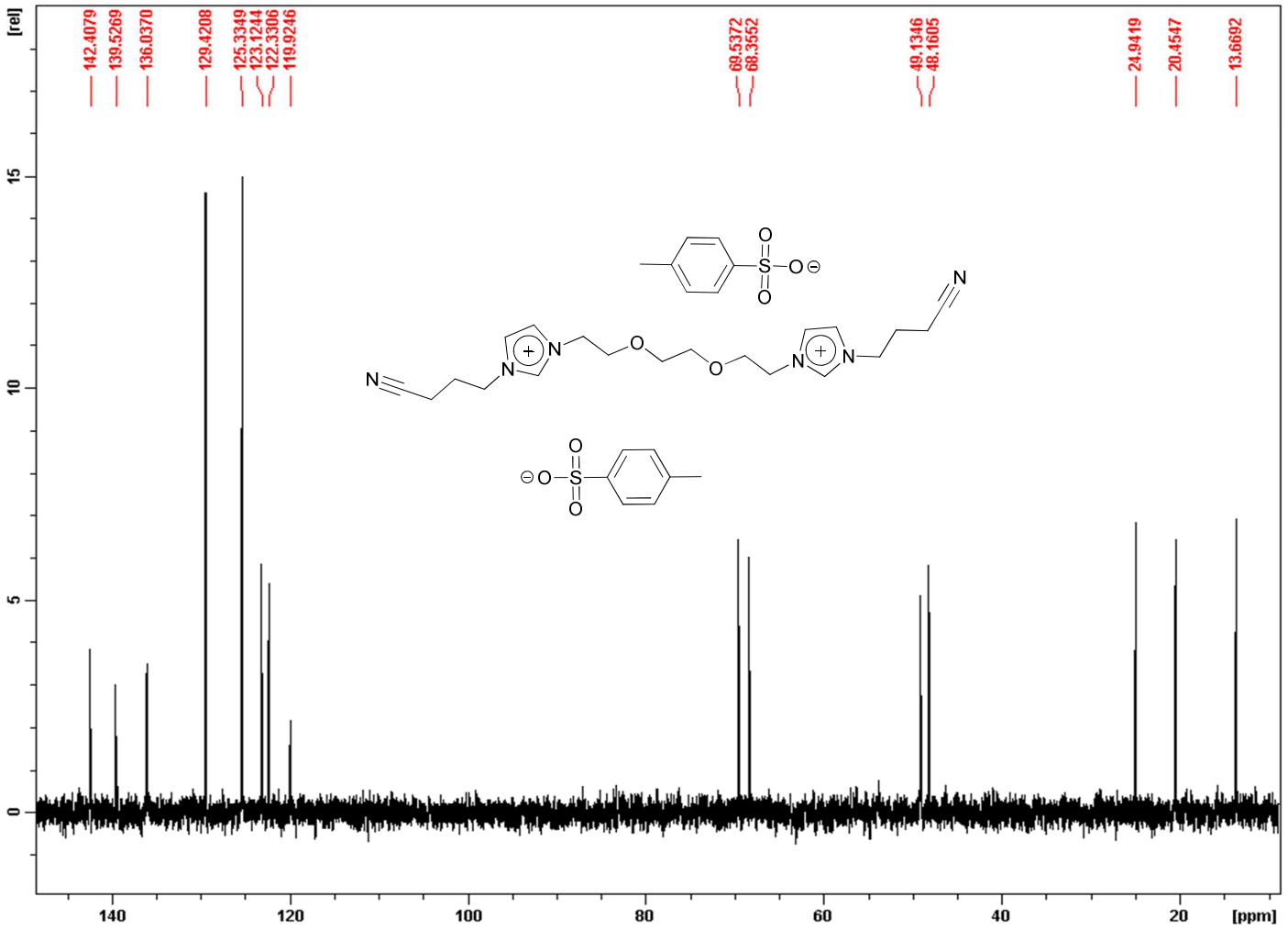

Figure S14 ^{13}C NMR spectrum of 1,8-Bis[1-(3-cyanopropylimidazolium-1-yl)]-3,6-dioxaoctane di(p-toluenesulfonate) (3).

References

(1) Bara, J. E. Versatile and Scalable Method for Producing N-Functionalized Imidazoles. *Ind. Eng. Chem. Res.* **2011,** *50*, 13614-13619.

(2) Lethesh, K. C.; Van Hecke, K.; Van Meervelt, L.; Nockemann, P.; Kirchner, B.; Zahn, S.; Parac-Vogt, T. N.; Dehaen, W.; Binnemans, K. Nitrile-Functionalized Pyridinium, Pyrrolidinium, and Piperidinium Ionic Liquids. *J. Phys. Chem. B* **2011,** *115*, 8424-8438.